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Waterless lithographic plates

Abstract:

PCT No. PCT/GB96/01973 Sec. 371 Date Feb. 11, 1998 Sec. 102(e) Date Feb. 11, 1998 PCT Filed Aug. 13, 1996 PCT Pub. No. WO97/07986 PCT Pub. Date Mar. 6, 1997A method for preparing a waterless lithographic plate is disclosed. A mixture that contains a water-repellant release material and a compound that becomes aqueous developable on heating is coated on a support, heated imagewise, and developed to produce the printing plate. Preferred water-repellant release materials are acrylic and methacrylic polymers with fluorinated side chains and silicone containing polymers, especially organo functional siloxanes. Preferred compounds that become aqueous developable on heating are phenolic resins as well as complexes of phenolic resins with quinolinium compounds, benzothiazolium compounds, pyridinium compounds, and imidazoline compounds.

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(57) Abstract

There is described a method of preparing a water-less lithographic plate which comprises a support having an oleophilic surface there being coated on the oleophilic surface a mixture which comprises as one component an ink-repellent and water-repellent release material or a mixture of such materials, and as the other essential component a water-insoluble photosensitive composition which is rendered aqueous developable by light exposure, or a water-insoluble composition which is rendered aqueous developable by heat, the ratio of release material to water-insoluble composition in the mixture being from 20 to 80 release material to 80 - 20 water-insoluble composition by weight, imagewise treating the mixture on the support, developing the mixture with an aqueous alkali solution to render the treated areas of the water-insoluble composition water-soluble and to remove this composition together with the release material, to expose the oleophilic surface of the support in the treated areas of the plate and leaving the release material and the water-insoluble composition in the untreated areas of the plate so yielding a negative working water-less lithographic plate.

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Water-less Lithographic Plates

This invention relates to the production of so-called water-less lithographic plates.

Lithographic plates may be divided into two classes. Those which require dampening water which is fed to the non-image areas of the plate, forms a water film and acts as an ink-repellant layer; this is the so-called fount solution and those which require no fount solution are called driographs or water-less lithographic plates. Most lithographic plates at present in use are of the first type and require a fount-solution during printing. However, lithographic plates of this type suffer from a number of disadvantages. Some of these are:-

a) adjustment of the proper ink-water balance during press operation is difficult and requires great experience. If the correct ink-water balance is not achieved scumming is occasioned when the printed ink image extends into the non-image areas ruining the printed image.

b) adjustment of the ink-water balance at start-up or re-start up is particularly difficult and can not be stabilised until a large number of sheets have been printed, thus incurring waste,

c) the ink tends to become emulsified which leads to poor adherence of the ink on to the plate which causes problems in colour reproduction and in dot reproduction,

d) the printing press has to be provided with a dampening system, thus increasing its size and complexity. These dampening solutions contain volatile organic compounds.

e) The plate care chemistry and fount solutions require careful control and selection. Further plate cleaners contain significant levels of solvent which is not desirable.

However, with water-less plates in which the ink-releasing layer is, for example, a cured silicone layer there is no scumming and clearer images can be produced. Very often water-less plates comprise a base material, for example aluminium plate, on which a photosensitive layer is coated, on this photosensitive layer there is coated a silicone layer. After imagewise exposure and development in which selected areas of the photosensitive composition are altered, the overlying silicone layer is removed and the plate is inked up. The ink adheres only to those areas of the plate not covered by the silicone remaining after development. Thus the plate can be printed without the need to use a fount solution.

However, in practice it has proved difficult to get the silicone layer composition to adhere to the photosensitive layer. In spite of the idea of water-less plates having been described in patent specifications for at least fifteen years very little has been done to commercialise the idea and water-less plates which have been and are being sold are more expensive than the conventional plates which require a fount solution.

According to the present invention there is provided a method of preparing a water-less lithographic plate which comprises a support having an oleophilic surface there being coated on the oleophilic surface a mixture which comprises as one component an ink-repellent and water-repellent release material or a mixture of such materials, and as the other essential component a water-insoluble photosensitive composition which is rendered aqueous developable by light exposure, or a water-insoluble composition which is rendered aqueous developable by heat, the ratio of release material to water-insoluble composition in the mixture being from 20 to 80 release material to 80 - 20 water-insoluble composition by weight, imagewise treating the mixture on the support,

developing the mixture with an aqueous alkali solution to render the treated areas of the water-insoluble composition developable and to remove this composition together with the release material, and so to expose the oleophilic surface of the support in the imagewise treated areas of the plate and leaving the release material and the water-insoluble composition in the untreated areas of the plate so yielding a negative working water-less lithographic plate.

The preferred water-repellent material is a fluorinated resin or polymer. Preferably the fluorinated resin or polymer is a polymerisation product of an acrylic or methacrylic monomer having a perfluoroalkyl group in a side chain. At least one other copolymerisable monomer may also be present.

Commercially available fluorine resins or polymers are available on the market as "ASAHI GUARD AG-710" (manufactured by Asahi Glass Co., Ltd), "ASAHI GUARD AG-550" (manufactured by Asahi Glass Co. Ltd), "DICGURARD F-60" (manufactured by Dainippon Ink and Chemicals, Inc.), "DICGURARD F-70" (manufactured by Dainippon Ink and Chemicals, Inc.) "SCOTCH GUARD FC-282" (manufactured by Sumitomo 3M), "ZEPEL B" and 'Zonyl 8070' (both manufactured by E.I. DuPont). Examples of the perfluoroalkyl-bearing monomer are (perfluorononyl)ethyl acrylate, (perfluorononyl)ethyl methacrylate, (perfluoroisononyl)ethyl acrylate, (perfluoroisononyl)- ethyl methacrylate, (perflurooctyl)ethyl acrylate, (perfluorooctyl)ethyl methacrylate, (perfluoroheptyl)ethyl acrylate, (perfluoroheptyl(ethyl methacrylate, etc. Examples of the other copolymerisable monomer which may be present include styrene, acrylonitrile, acrylic acid and methacrylic acid, and their esters such as alkyl esters (e.g. methyl ester, ethyl ester, propyl ester, butyl ester, isobutyl ester, 2-ethylhexyl ester, hexyl ester, decyl ester, lauryl ester, stearyl ester), hydroxyalkyl esters (e.g. ß-hydroxyethyl ester) and glycidyl ester. The proportion of these monomers may be optionally selected, but the amount of the

perfluoroalkyl-bearing monomer should be not less than 50% by weight on the basis of the amount of the entire monomers.

These fluorine resins are described in US 4508814 to Nippon Paint which describes a process wherein a water-soluble photosensitive compound is used to prepare either a negative working plate or a positive working plate.

Other suitable fluorine resins are described in US 4087584 and in US 4724195.

Suitable silicones for use in the present invention are described in for example US 4510277, US 3865588, US 5266443 and US 4874686.

Examples of useful silicone polymers are organo functional siloxanes. One such siloxane is available from Dow Corning as a 40% solids emulsion under the designation SYL OFF 7920.

Usefully a curing catalyst may be used in conjunction with the ink-releasing composition. For example, a platinum based catalyst marketed by Dow Corning under the designation SYL OFF 7922 may be used to cure SYL OFF 7920.

A mixture of fluorine resin and silicone may be used.

A suitable by weight ratio is from 80-20 fluorine resin to 20-80 silicone.

As the water-insoluble compound which is rendered water-developable by light exposure there may be used any of the compounds used to prepare direct positive lithographic plates.

For example a composition which comprises an alkali-soluble phenolic resin and an onium salt as described in US 4708925 may be used.

However preferably the water-insoluble composition which is rendered water-developable by light exposure is a composition which comprises a o-quinone diazide compound.

Examples of particularly preferred o-quinone diazide compounds are disclosed in a variety of publications such as U.S. Pat. Nos. 2,766,118; 2,767,092; 2,772,972; 2,859,112; 2,907,665; 3,046,110; 3,046,111; 3,046,115; 3,046,118; 3,046,119; 3,046,120; 3,046,121; 3,046,122; 3,046,123; 3,061,430; 3,102,809; 3,106,465; 3,635,709 and 3,647,443 and these compounds may preferably be used in the invention. Among these, particularly preferred are o-naphthoquinonediazidosulfonates or o-naphthoquinonediazidocarboxylates of aromatic hydroxyl compounds; o-naphthoquinonediazidosulfonic acid amides or o-naphthoquinonediazido-carboxylic acid amides of aromatic amine compounds, for instance, esters of benzoquinone-1, 2-diazidosulfonic acid or naphthoquinone-1,2- diazidosulfonic acid with polyhydroxyphenyl (hereinafter the term "ester" also include partial esters); esters of naphthoquinone-1,2- diazido-4-sulfonic acid or naphthoquinone-1,2-diazido-5-sulfonic acid with pyrogallol/acetone resins; esters of benzoquinone-1,2- diazidosulfonic acid or naphthoquinone-1,2-diazidosulfonic acid with novolak type phenol/formaldehyde resins or novalak type cresol/formaldehyde resins; amides of poly(p-aminostyrene) and naphthoquinone-1, 2-diazido-4-sulfonic acid or naphthoquinone-1,2- diazido-5-sulfonic acid; esters of poly(p-hydroxystyrene) and naphthoquinone-1,2- diazido-5-sulfonic acid; esters of polyethylene glycol with naphthoquinone-1,2-diazido-4-sulfonic acid or naphthoquinone-1, 2-diazido 5-sulfonic acid: amides of polymeric amines with naphthoquinone-1,2-diazido-4-sulfonic.

Preferably the imagewise light exposure is carried out to U.V. light by a contact exposure of the negative transparency located in close contact with the plate.

As a suitable heat sensitive substance there may be used a polymeric substance which is water-insoluble when coated as a layer but which when heated is aqueous developable. Such polymeric substances are described in our co-pending application GB. 9614693.1 which was filed on the 12th July 1996.

In these polymeric substances when they are heated there is merely a change in the solubility differential of the unheated polymeric substance and the heated polymeric substance. In the heated areas the polymeric substance is dissolved away.

Most preferably the polymeric substance is a phenolic resin. The term phenolic resin will be used hereinafter but it is to be understood that other suitable polymeric substances may be used.

The coated plate may be heat imaged using a stylus or any other instrument in which the heat can be directed imagewise.

However, preferably there is coated on the support in addition to the initially developer insoluble phenolic resin a laser-radiation absorbing material and the support is exposed to a laser to heat the coating imagewise.

Most preferably the laser-radiation absorbing material absorbs infra-red radiation and the laser used emits radiation at above 600nm.

Usefully the laser-radiation absorbing material is carbon black. Alternatively the laser-radiation absorbing material is an infra red absorbing dye.

In one preferred method of the present invention there is coated on the support in addition to the initially developer-insoluble phenolic resin and the laser-radiation absorbing material a compound which forms a thermally frangible complex with the phenolic resin.

The complex of the developer-insoluble phenolic resin and the compound which forms a thermally frangible complex with the phenolic resin is less soluble in the developer solution than the uncomplexed phenolic resin. However when this complex is imagewise heated the complex breaks down so allowing the non-complexed phenolic resin to be dissolved in the developing solution. Thus the solubility differential between the heated areas of the phenolic resin and the unheated areas is increased when the phenolic resin is complexed.

A large number of compounds which form a thermally frangible complex with the phenolic resin have been located. Examples of such compounds are quinolinium compounds, benzothiazolium compounds, pyridinium compounds and imidazoline compounds.

Examples of suitable quinolinium compounds are 1-ethyl-2-methyl quinolinium iodide, 1-ethyl-4-methyl quinolinium iodide and cyanine dyes which comprise a quinolinium moiety.

Examples of suitable benzothiazolium compounds are 3-ethyl-(-2 3-ethyl-2(3H)-benzothiazolylidene)-2-methyl-1(-propenyl) benzothiazolium cationic dyes and 3-ethyl-2-methyl benzothiazolium iodide.

Examples of suitable pyridine compounds are cetyl pyridinium bromide and ethyl viologen dications.

Examples of suitable imidazole compounds are Monazoline C, Monazoline O, Monazoline CY and Monazoline T all of which are manufactured by Mona Industries.

Preferably the laser radiation absorbing material is one whose absorption spectrum is significant at the wavelength output of the laser which is to be used in the method of the present invention.

Preferably the laser emits at above 600nm as at these wavelengths a significant amount of localised heat is produced.

The laser radiation absorbing material may be carbon such as carbon black or graphite. It may be a commercially available pigment such as Heliogen Green as supplied by BASF or Nigrosine Base NG1 as supplied by NH Laboratories Inc. Usefully it may be a dye or pigment of the squarylium, merocyanine, indolizine, pyrylium or metal dithioline classes.

The method of the present invention yields a negative working water-less lithographic plate in which the composition remaining on the plate constitutes the oleophobic or ink releasing areas of the plate, whilst the areas of the plate from which the photosensitive or heat-sensitive composition was removed by development constitutes the oleophilic areas of the plate.

After the development step and drying, the plate can be inked up. The ink is held in the areas between the portions of ink releasing composition which remain on the plate. No fount solution is required to differentiate between the oleophilic and the ink releasing

areas of the plate when printing using an oleophilic printing ink. The oleophilic base used in the method of the present invention is preferably an aluminium plate which will carry on its surface a thin aluminium oxide layer due to action with atmospheric oxygen. This layer may be of increased thickness due to anodising treatment of the base. Post anodic treatment of the base to increase its oleophilicity may be undertaken. Optionally electrochemical etching may precede these processes to improve adhesion between substrate and coating.

Alternatively or in addition the aluminium base may have been coated with a layer which gives the coated base improved oleophilicity over the uncoated base. Examples of such coatings are an oleophilic polymer for example ethyl cellulose, a resol type resin, a polychloroprene or a polyacrylonitrile-butadiene copolymer.

The coating over the aluminium base plate whether treated or not may be a so-called primer layer as described for example in E.P. 44220, US 5061598 and E.P. 560347. Such primer layers may comprise a large variety of polymers such as polyester, polyurethanes and polyamides and help to provide a better printing surface than is afforded by uncoated aluminium.

Another base material which may be used in the method of the present invention is a plastics material base or a treated paper base as used as a base in the photographic industry. A particularly useful plastics material base is polyethylene terephthalate which has been subbed to render its surface oleophilic. A so-called resin coated paper which has been corona discharge treated may also be used.

A particularly useful photosensitive positive working composition comprises a naphthoquinone diazide sulphonic acid ester of a phenol resin. These esters are formed from a soluble phenolic resin such as those described in E.P. 196031. Ortho-quinone

diazido sulphonic acid/halides such as 1,2-benzoquinone-2-diazido-4-sulfonylchloride, 1,2-naphthoquinone-2-diazido-4-sulfonylchloride, and 1,2-naphthoquinone-2-diazido-5-sulfonylchloride.

The condensates between sulfonylhalides, e.g., o-quinonediazido sulfonylchloride and the phenolic resin may be prepared as described in E.P. 196031.

In addition triarylmethane dyes and triazine acid generators may be present in the compositions. Examples of suitable triazine acid generators are given in E.P. 271195.

A composition which comprises 2,1,4 napthaquinone diazide sulphonic ester of a novalac resin and 2-(4-thiomethyl-phenyl)-4,6-bis- (trichloromethyl)-1,3,5- triazine is hereinafter referred to as photosensitive positive working photosensitive composition A.

An example of a developing solution used in the development step is an aqueous solution of 8% metasilicate, 0.1% of an organic phosphite ester of an ethoxylated alcohol and 0.01% of polyoxy propylene methyl ethyl ammonium chloride. This is hereinafter referred to as Developing solution A.

It is to be noted that the water-less lithographic plate prepared by the method of the present invention is a negative working plate. As the light-sensitive or heat-sensitive composition used is a positive working composition it would be thought that a positive working plate would be prepared. The fact that a negative plate is prepared is entirely unexpected. On development it appears that the aqueous alkali developing solution in the treated areas removes both the water-insoluble composition and the water-repellent polymer to reveal the oleophilic surface of the support. Even though the unexposed areas of the plate comprised a high level of water-insoluble composition these areas did not accept ink even though it would be expected that they should.

The accompanying Examples will serve to illustrate the invention.

Example 1

On to a grained oleophilic aluminium plate there is applied a coating composition which comprised 2g of Asahi Guard A.G. 550 a fluorinated resin manufactured by Asahi Glass Co Ltd, 0.6g of the positive working photosensitive composition A, the coating composition being dispersed in 0.2g of oxitol. After the coating composition had been dried it was exposed to UV light through a negative. Thereafter the plate was developed for 2 minutes in developing solution A at 20°C.

In the exposed areas of the plate the developing solution was found to have removed both the water-insoluble composition and the water-repellent polymer to reveal the oleophilic surface of the support.

The thus formed negative working printing plate was inked-up and used on a printing press as a water-less plate requiring no fount solution. Several hundred good prints were obtained with good resolution using this plate.

Example 2

On to a grained oleophilic aluminium plate there was coated a coating composition which comprised 1.6g of SYL OFF 7920 a silicone compound marketed by Dow Corning, 0.4g of SYL OFF 7922 a curing catalyst also marketed by Dow Corning, 0.8g of the positive working photosensitive composition A, this composition being dispersed in 0.2g of 2-ethoxyethanol. After the composition had been dried it was exposed to UV light through a mask. Thereafter the plate was developed for 2 minutes in developing solution A at 20°C.

After development a negative working plate was obtained from which more than 500 prints of good resolution were obtained using no fountain solution after inking the plate.

Example 3

On to a grained aluminium plate which had been coated with a thin layer of polychloroprene to increase its oleophilicity there was a coating composition which comprised 0.75g of Zonyl 8070, (a fluorinated resin marketed by Du Pont), 0.24g of SYL OFF 7920, 0.06g of SYL OFF 7922, 0.32g of the positive working photosensitive composition A, this composition being dispersed in 0.5g of 2-butanone.

After the composition had been dried it was exposed through a mask to U.V. light. Thereafter the plate was developed for 2 minutes in developing solution A at 20°C.

After development and drying, the negative plate was placed in a printing press and inked-up. More than 1000 prints of good resolution were obtained.

Example 4

UV Sensitised Onium Salt Containing Negative System.

A solution of the below composition was coated onto a piece of grained and anodised aluminium and dried at 100°C for one minute.

Composition

0.04g of 100% diphenyliodonium hexafluorophosphate.
0.50g of 20% w/w solids of novalak resin (LB744, Bakelite) in 1-methoxy-propan-2-ol.

0.22g of 100% polydimethylsiloxane vinylmethyl terminated.

0.043g of 100% (30-35%) methylhydro (605-70%) dimethylsiloxane copolymer.

0.40g of 1-methoxy-propan-2-ol.

0.5g of N-methyl pyrrolidone.

2.0g of methylethylketone.

0.01g of platinum-divinyl-tetramethyldisiloxane complex at 0.075% in xylene was added just before coating.

The plate produced was exposed to UV radiation through a mask and developed with developer solution A, so that the exposed areas were removed by the developer and the unexposed release areas remained.

On inking with waterless ink a negative image was seen.

When the inked-up negative plate was placed on a printing-press more than 1000 prints of good resolution were obtained.

Example 5

Onto a grained oleophilic aluminium plate was coated an IR sensitive composition as follows:

0.54g	LB6564 a phenol cresol novalac resin supplied by Bakelite.
0.06g	NK1144 an IR dye.
0.106g	Polydimethyl siloxane vinyl dimethyl terminated.
0.054g	(30-35%) Methylhydro (65-70%) dimethyl siloxane co-polymer.
1 drop	Platinum divinyltetramethyldisiloxane catalyst, 3% in xylene.
2.43g	N-methyl pyrrolidone.
2.43g	MEK

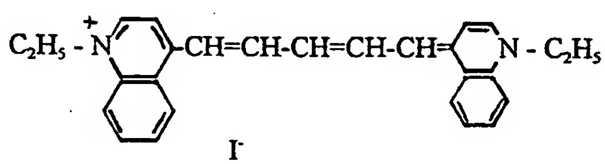
After this composition had been coated it was dried at 100°C for 2 minutes and exposed to an 830nm IR laser. The plate was then developed in developing solution A at 20°C.

In the exposed areas of the plate the developer was found to have removed the coating to reveal the oleophilic surface of the support.

The sensitivity of the plate was calculated to be at 83mJ/cm^2 or lower.

The negative plate was placed in a printing press and inked-up. More than 1000 prints of good resolution were obtained.

Dye NK1144 has the structure:-



Claims:-

1. A method of preparing a water-less lithographic plate which comprises a support having an oleophilic surface there being coated on the oleophilic surface a mixture which comprises as one component an ink-repellent and water-repellent release material or a mixture of such materials, and as the other essential component a water-insoluble photosensitive composition which is rendered aqueous developable by light exposure, or a water-insoluble composition which is rendered aqueous developable by heat, the ratio of release material to water-insoluble composition in the mixture being from 20 to 80 release material to 80 - 20 water-insoluble composition by weight, imagewise treating the mixture on the support, developing the mixture with an aqueous alkali solution to render the treated areas of the water-insoluble composition water-soluble and to remove this composition together with the release material, to expose the oleophilic surface of the support in the treated areas of the plate and leaving the release material and the water-insoluble composition in the untreated areas of the plate so yielding a negative working water-less lithographic plate.

2. A method according to claim 1 wherein the water-repellent release material is a fluorinated resin.

3. A method according to claim 2 wherein the fluorinated resin is a polymerisation product of an acrylic or methacrylic monomer having a perfluoroalkyl group in a side chain.

4. A method according to claim 3 wherein at least one other copolymerisable monomer is also present.

5. A method according to claim 1 wherein the water-repellent release material is a silicone.

6. A method according to claim 5 wherein the silicone is an organo functional siloxane.

7. A method according to claim 6 wherein a platinum curing catalyst for the siloxane is present.

8. A method according to claim 1 wherein the water-repellent release material is a mixture of a fluorinated resin and a silicone.

9. A method according to claim 1 wherein the water-insoluble photosensitive composition is an alkali-soluble phenolic resin and an onium salt.

10. A method according to claim 1 wherein the water-insoluble photosensitive composition is an o-quinone diazide compound.

11. A method according to claim 1 wherein the water-insoluble heat sensitive composition is a polymeric substance which is water-insoluble but which when heated is aqueous developer soluble.

12. A method according to claim 11 wherein the polymeric substance is a phenolic resin.

13. A method according to claim 1 wherein the coated plate is heat imaged using a stylus or other instrument in which heat can be directed imagewise.

14. A method according to claim 1 wherein there is present in the heat-sensitive composition a laser-radiation absorbing material and the support is imagewise exposed to a laser to heat the coating imagewise.

15. A method according to claim 14 wherein there is present in the heat-sensitive composition in addition to the initially developer-insoluble phenolic resin and the laser-radiation absorbing material a compound which forms a thermally frangible complex with the phenolic resin.

16. A method according to claim 15 wherein the compound which forms a thermally frangible complex with the phenolic resin is a quinolinium compound, benzothiazolium compound, a pyridinium compound or an imidazoline compound.